

Carbon Materials and Manufacturing
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Lecture - 34
Melt Spinning of Petroleum Pitches

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Melt Extrusion (or Melt Spinning)

Parameters: Viscosity, temperature, pressure

Extruder

Flow rate

Dropdown

Spinneret

Quenching

Cross Flow Air

Winding

Spinneret top-view

Coal tar pitch

Basic melt-extrusion set-up

- Material is melted inside an extruder above its glass transition temperature.
- Melt is pumped into a spin chamber, which contains a filter to remove solid particles.
- Bottom of this chamber contains multiple capillaries.
- Extruded fibers are cooled by air and collected/ wound.
- Viscosity of material is controlled by melting temperature.
- Commonly used for pitch or polymer melts.
- Extruded fibers typically have diameters in the 5-10 μm range.

The first method of manufacturing carbon fibers: we are going to discuss Melt Spinning or Melt Extrusion here. This is how the basic setup looks like. You can see that this is an extrusion process. What is an extrusion? You melt a polymer, this is typically used for polymers and plastics. You basically melt a polymer and then you give it a certain shape and then you cool it down, that is the extrusion process.

You have a certain extruder but the only difference is that if you are making plastic bottles, you have a different kind of mold for it and you are blowing air inside it. You have different types of shapes, you have different types of molds. What kind of mold will you have for making fibers?

You need to have something known as this spinneret, which has nothing but a lot of capillaries and then your material flows through it and you get fibers. This is the basic principle and this is a very simple process right. This is just melt spinning.

This is performed especially petrochemical precursors such as pitches and you can also use it for melted polymers. So, let me just detail these steps again. First of all you melt your material above its glass transition temperature. Now, glass transition temperature is a very important concept.

What is glass transition? I think we also talked briefly talked about it during photolithography lectures. Glass transition temperature is the temperature below which the material behaves like a glass. Above this, the material is sort of melted. I do not even know melting is the right term that we should use for polymers.

There is little bit the flow of fluid or flow of chains or molecules of polymers. It has a slightly different mechanism compared to other for example melted metals this is what makes polymers very interesting. There is entire polymer chemistry, polymer engineering courses; you can learn about the properties of polymers. But there are few properties that we are definitely going to discuss here because they are important for fiber fabrication.

One of them being the glass transition temperature and the other one is what is known as viscoelasticity. And we are going to separately learn about these techniques because viscoelasticity becomes important for both melt spinning and electro spinning. So, any kind of spinning techniques when you want to pull fibers, if you think about it, what is the property that you need in any material to be able to pull fibers?

You need the material to be elastic to some extent; but at the same time carbon is hard and brittle. But the polymer that we use for spinning, they need to be elastic. But is it just elasticity or there is something else? Because we also do not want something which has no viscosity, whatsoever for a reason.

So, we will talk about these properties. The first thing we do in this setup is we heat the material above its glass transition temperature. Now, that becomes sort of processable material. Now, you can process it. Now, you can pull fibers. How do you do that? You pump this polymer or pitch into what is known as the spin chamber.

First thing you need to do is you need to remove if there are any particles. Because if you have any particles, in the case of fibers, they can be catastrophic. You will get these

bulges between the fibers because of your crystals and that might also damage mechanically damage your entire fiber.

So, first thing is that you need to remove if there are any particles. Now, that does not necessarily mean that you have impurities; sometimes you may also have certain particles of the polymer itself which is basically the polymer that still does not have a free flow. So, you need to remove those kinds of sort of bigger chunks of material.

So, you will pass it through some filtration unit and after that, what you have is this spinneret. I have also shown a cross-sectional view or the top view of this spinneret. What do you have? You have a lot of holes and these holes are basically capillaries, through these capillaries your polymer can pass.

So, this is basically the idea. Now, you will of course have sort of very high chambers. You will collect the fiber somewhere in the bottom. This distance is where you want to cool down your fibers. So, you can do quenching. You can basically just cool it down. So, you may have a cooling chamber.

What will happen when you cool down the polymer? Now, that temperature is below its glass transition temperatures. So, now, it will become hard. And that is what you wanted. So that once you get the fibers, you do not want them to break further. You do not want them to change their shape further. You want to make them glass like, you want to make them hard.

So, you can do the quenching or cooling or you can also perform this cooling just by air. You can blow air, which will also help your fibers to stay away from each other; not sort of agglomerate or not form one big chunk of polymers.

So, this needs to be done very soon after they come out of the extruder otherwise, they will stick to each other. So, you need to basically do quenching or air cooling. In these kinds of industrial setups, you will typically have a cross-flow of the air for cooling the fibers. And as you can see, at the bottom, you have a fiber collection unit and typically, you are winding the fibers.

So, you have these fiber winding units and as soon as they dry up, you can collect them and that is how you perform the melt spinning process. Now, as already I mentioned that

this method commonly used for pitch, but you also can use it for melted polymers. Why am I saying this? Because you will say that polymer should always be melted when you are performing any spinning.

Yes, it should not be, but the term melted is not necessarily correct because they can just be solutions that are liquid at room temperature. So, for those kinds of polymers means you would do electro spinning with them rather than melt extrusion. Melt is specifically for melted polymers.

Now, these kinds of polymers typically that are fabricated using this process will have their diameters in the micrometer range. You will not get nanofibers using that spinning. You can imagine that for making nanofibers or very thin fibers, you will need to have very small capillaries and then the surface tension of the capillary becomes very important. You have a viscous liquid and very small capillary, then it becomes very difficult to have very thin diameters.

So, typically these kinds of fibers, you will have in the 5 to 10 micrometer range or even larger. So, 5 to 10 micrometers what you will typically get after their carbonization or slightly smaller than that. The shrinkage patterns in the case of fibers are also different from what you have for bulk industrial carbons because there you have much more shrinkage due to much more mass loss.

Here, you have much more surface area. So, your defects or byproducts can anneal out easily and you do not get as much shrinkage as you would get in the case of bulk materials and we are going to discuss also why that happens. This is a picture of the coal tar pitch.

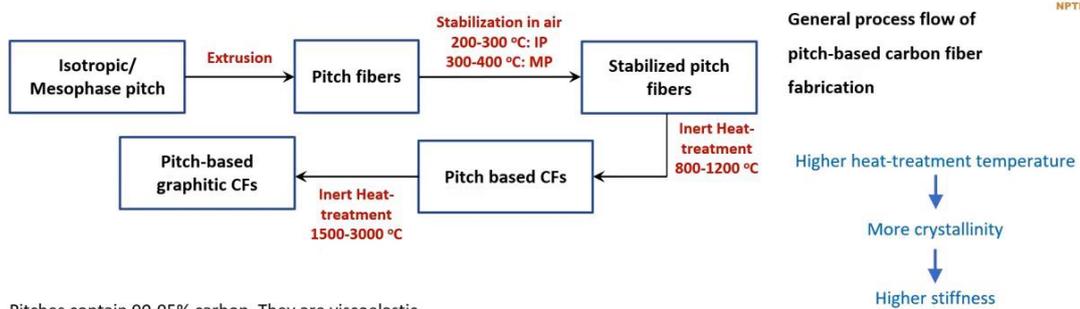
I just took it outside somewhere on a hot day just to again give you an idea of what is pitch. This is highly viscous material that you get on the roadsides on a hot day. It is not very difficult in India to get these kinds of pictures. It is a beautiful material. It is a very high carbon-containing material, it has this beautiful shine, and it has very good viscoelasticity.

You can already see, you touch it and you will know that you can pull fibers out of it. So, this is one of the most common or one of the oldest carbon precursors in the case of fibers.

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Melt Extrusion (or Melt Spinning)



- Pitches contain 90-95% carbon. They are viscoelastic.
- **Viscoelasticity:** Material exhibits both elastic (similar to solids) and viscous (similar to liquids) deformation. Deformation is dependent not just on strain but also on strain rate.
- Viscosity of the material is controlled by melting temperature.
- After spinning, fibers are heat-treated to ~1000 °C for carbonization. In case of graphite fiber production (from mesophase pitch), heat-treatment is performed up to 3000 °C.
- Additives can be mixed in the pitch to obtain higher crystallinity.



Let us talk a little bit more about the pitch-based carbon fiber fabrication. This is a process flow because this is the industrial process used very commonly that you should know about it. Isotropic or mesophase pitch, you will take any type of petroleum pitch and then, you will perform the extrusion as I have shown previously using this spinning setup.

Now, you have pitch fibers. What do you do with pitch fibers? Do you directly carbonize them? Now, there is one more stabilization step in between. So, this stabilization is performed in air. For isotropic pitch, you perform it at between 200 to 300 °C and slightly higher temperatures for mesophase pitch.

Stabilization is typically performed to get rid of the undesired organic material; some of it at least and you are performing it in air which means you are open to burning those things out. So, any volatile organic materials will typically burn out; only the heavier hydrocarbons which are high in carbon content, will stay there. That is why you perform the stabilization.

Also, this stabilization step leads to a little bit of cross-linking between your heavy hydrocarbon type molecule. So, you then get less porosity in your fibers and you get good quality solid fibers. you need to perform this stabilization of pitch and afterward you perform your regular heat treatment.

Now, when I say regular heat treatment, it depends on what is the crystallinity that you want in your final fiber? So, mesophase pitch will give you almost polycrystalline graphite-like fibers. Although, they may have different kind of structural arrangement. These graphite sheets may not be as nicely. You do not imagine these polycrystalline materials that I have shown that you have these random orientations, that is a possibility.

But that is not the only one possible microstructure. So, we are also going to discuss what are the possible ordering? What kind of stacking of sheets that you get in these graphitic fibers, but that is only from the mesophase pitch. You can also get from isotropic pitch.

So, first you perform the heat treatment at relatively low temperatures, between 800 and 1200 and you can actually also stop at that point if that is the desired carbon material. In industrial applications, you do not really care for very high purity of carbon fibers

Now, you can perform the heat treatment further. You can go all the way up to 3000 °C as in the case of graphite and you can get really high purity of the fibers. You can also get much higher Young's modulus good stiffness of the polymers.

But of the carbon fibers, but is that what you need sometimes it is not the stiffness, but rather the flexibility, rather the tensile strength of the fiber that becomes more important for you. Purity; how much purity is acceptable to you? Depending upon that you will also need to see how much cost is going to be increased because 3000 °C heat temperature is very energy-consuming.

If it is acceptable for you to have the fibers at a slightly lower temperature, you might want to stop there. But if you definitely need very high-quality carbon fibers, then you will go all the way to 3000 °C. Again, in similar types of furnaces that you would use for graphite manufacturing.

So, this is the process flow of pitch-based fibers. Some important things about pitch are that most of the pitches have their purity between 90-95 percent, a little bit higher can be also possible. They have this special property known as viscoelasticity. As I mentioned before, we are going to dedicate some time to viscoelasticity; but briefly, the definition of what is viscoelasticity.

As the name itself suggests this material has both viscosity and elasticity. Elasticity is a property of solid materials. Elasticity means if you deform the material, it will come back to its normal place as soon as you leave it like a rubber band that is the elastic property. That is a property of solids. Viscosity is a property of liquids. This is the resistance to the applied force that the liquid offers.

Now, this polymer type of materials or heavy hydrocarbons like pitch, these materials offer the properties of both solids and liquids. So, they have both viscosity element and the elasticity element. How is that possible? Polymers have these long chain-like molecules. In the case of pitches, you have hydrocarbons that are chain-like molecules or in some cases sheet-like molecules.

Now, these chains can entangle. They can form these very structures that are very difficult to open. They are entangled chain like structures; but at the same time, they may also have some chains that are floating or that are able to freely flow, not all of them, but some of them.

So, you have partially solid-like properties. Similarly, in the case of semi-crystalline materials or in the case of liquid crystal-like materials such as mesophase pitch, there are certain parts that are crystalline. These crystalline parts behave like solids and can offer elasticity, while the liquid-like parts will offer resistance to flow.

That is why you have a combination and that combination can by the way be very complex, not all polymers will have the same viscoelastic properties. Because well not all polymers are semi-crystalline and the size the length of chains in different polymers is different; some of them have very short chain, some have very long chain.

So, depending upon all of these factors, you will have different viscoelasticities in various polymers. But viscoelasticity is very important in order to be able to pull fibers out of something. Because if it is a liquid, just a liquid not elastic at all, if it has only viscosity let us take an example of water, difficult to pull water fibers out of water.

So, we definitely need elasticity; but we also need some viscosity. We do need some liquid-like properties because if it is a solid material, just a crystalline material, then also it is not possible to pull fibers out of it.

So, viscoelasticity is a very interesting property that pitches and that a lot of polymers also have. In fact, you can also control the length of the chains, you can also control how much solvent you have in a certain polymer solution. So, based on that, you also sort of tune the viscoelasticity a little bit for manufacturing fibers.

Now, in the case of pitch-based fabrication or the melt spinning, you would typically also control the viscosity to some extent by the melting temperature. Because here you want to have a certain viscosity in your liquid which is just optimum for giving the fibers. and the diameters of the fibers can be controlled by this viscosity.

So, you can imagine that if your material has water-like properties, then you will not be able to pull fibers; but it is slightly thicker than water, slightly more viscous than water, then you are able to pull fibers. But they might be very thin fibers. Thin fibers, how long can they be? How long is their aspect ratio? What is the possibility there? That we need to optimize.

And then, if you have these very viscous fluids like honey, then you can pull fibers. But what is the minimum diameter you can get from these fibers? These are the things that are optimized for various materials that are being spun. in the case of pitch, we control it by controlling the chamber temperature. And then, as I have already mentioned, then you perform the heat treatment under environment.

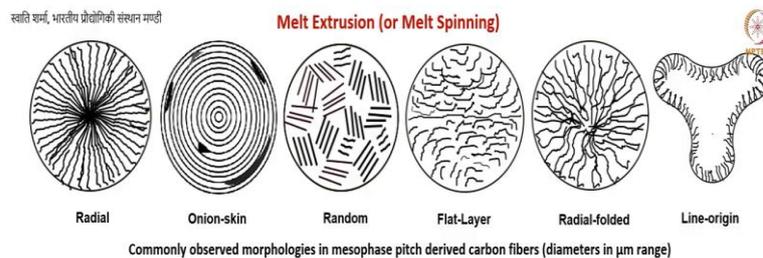
That is done after the stabilization step. If you need certain properties, for example, if you need very high crystallinity in your polymer; but you only have isotropic pitch available; you could potentially mix a few coke particles or some sort of carbon nanotubes.

These kinds of additives can be mixed inside your pitches before the fibers are pulled out of it. But of course, you need to remember that you need to have an optimum concentration of the additive and also the size of the additive because you remember that you were filtering out these solid particles. So, if you add bigger solid particles, then it will block the capillaries.

So, you need to have only very small additive, very thin in terms of size; but that is also possible. For all carbon materials, this is our golden rule: higher the heat treatment temperature, higher the crystallinity, higher the stiffness and when we say stiffness, we

are talking about Young's modulus. So, this is also valid for your fibers and this becomes a very important industrially important property because for many applications, what you need is good mechanical strength. So, that is why for carbon fibers, especially pitch-based fibers, the higher the heat treatment temperature would increase the cost of the fibers. So, this is basically a direct measure of the quality of your carbon fibers.

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- In graphite (or highly graphitic) fibers, crystallites can be organized in various ways depending upon the viscosity of the pitch, shape of the spinneret, quenching and drying conditions and heat-treatment conditions.
 - Heat-treatment is performed under inert atmosphere at $\leq 5^\circ\text{C}$ per minute ramp rates.
 - Fibers have a higher surface area compared to larger structures, so in principle they should be able to yield graphite at relatively lower temperatures.
 - But this is not always the case since the carbonization is done in bulk and the diameter is still in micrometer scale.
- Image redrawn from Edie, D.D. Pitch and mesophase fibers. In *Carbon Fibers Filaments and Composites*. Kluwer Academic Publ., Dordrecht, The Netherlands, 1990.
- Further reading: (i) M. Inagaki. *New Carbons: Control of Structure and Functions*. Elsevier, 2000.
(ii) D.D. Edie, J.J. McHugh. High Performance Carbon Fibers. In *Carbon Materials for Advanced Technologies*, 1999.



I told you that the microstructure of pitch-based carbon fibers especially mesophase pitch-based carbon fibers is very interesting. Mesophase is more interesting because we have graphite crystallites. You see these the six possible arrangements of these graphite crystallites.

The third one is the random orientation, which is what you would expect from other types of pitches as well. If you have isotropic pitch and you heat it up to 3000°C , you will get some graphitic content but that the graphitic crystallites will be randomly oriented.

Also, you will have some non-crystalline parts in between them. But if you have mesophase pitch, you will get very highly graphitic material, you will have very small fraction of non-graphitic carbon in that. So, we can call them graphite fibers. In fact, this

term is also industrially used. You will hear the word graphite fibers. Be careful sometimes industrial fibers; they are not really graphite; they are just graphitic.

But in the terminology, they call it graphite because that graphite sounds more sophisticated and also more costly. So, often the terminology is also used in the wrong fashion. Anyway, that is not our concern. For you, it is important to know what is graphite. For you, it is important to know that if you have very high crystallinity, then you can call it graphite fiber; not graphitic fibers.

From mesophase pitch when you get the fibers, you can have these various arrangements of the graphite crystallites. These are the pictures of the cross-sections of the fibers. So, the first one you can see all these graphite flakes are radially organized. That these things will by the way depend on your on at what speed, what temperature, what type of pitch you process. So, these are dependent on your manufacturing parameters as well as your carbonization parameters. So, it will depend on what is the heat treatment rate, what is the ramp rate at which you heated these polymers. Also, what is the highest temperature.

Second one you see is this radial kind of, so you have these concentric cylinders. This is the cross-section. You have onion-skin is what is the name that is used commercially, but this is the concentric cylinder type structure. Then, you of course have the random orientation. You can also have these small flakes; but flat like on top of each other, they are trying to organize themselves. So, they are just flat structure.

Then, again you can have radial structure but folded. So, you have graphite crystallites, but they are highly turbostratic. Turbostratic means they are not completely in AB AB A arrangement. So, in the case of carbon fibers, when we talk about graphite fibers, even when we use the term graphite, we may not have the perfect AB AB A organization. Here, we call fiber graphite, when it has just a very high graphitic content.

Even, so, you have the large L_a value, large crystallized size. L_c value is little bit tricky in the case of fibers because you do not have these perfect crystallites. In the case of random organization, you can probably calculate.

But in the case of radial or radial folded geometries or morphologies, you may not be able to calculate the L_c in the same way that you did for other crystallites. The point here is the L_a value becomes more important and the fact that you have a larger crystallinity

and less and less, very small to negligible non-crystalline parts, then you will call them graphite fibers. In many of these cases, your graphite sheets may not be perfectly organized on top of each other or maybe you will have the stack thickness.

Each of these lines that you see here, that is not necessarily one single graphite sheet. It may be a small stack of graphite sheets. But, however, they have certain curves. They are not perfect as in the case of HOPG. Now, the last one that you see, line origin that is something which you get if your spinner edge from where your fibers were extruded if that is not perfectly circular.

So, you may also have different shapes of the spinneret and you sometimes intentionally do that because you want to have higher surface area. You see if you have this kind of fiber shape, then you will be able to have more surface area in the fibers, so your by-products will anneal out more easily and for whatever application you are using, maybe this is a better geometry.

Also, other than these six structures, you can also have some other possible morphologies. Of course, if you change the shape of the spinneret, you can also make it flat ribbon-like fibers. So, there are many such options that are possible.

Typically, heat treatment is performed in all cases. In industrial cases, you perform the heat treatment is at less than 5 °C per minute that is your temperature ramp rate. And then, you will keep your material at the final heat treatment temperature for at least an hour. You can also do it for several hours because that also leads to better organization. In the case of fibers, you need to understand whether or not high Young's modulus is important.

So, if you are using these materials for making manufacturing purposes, often you need high stiffness. But not all the time, let us say if you are making biomedical implants, you may need also a little bit of flexibility, so that when your tissue is growing on top of bone-implant, then the tissue is able to press it a little bit and that is why you may not need very high crystallinity.

But that depends on your application. Even in the case of bone implants, it depends on whether you are making the load-bearing joints of your body or other joints of your body

or you are making also a tissue implant, ligament implant, or ligament template on which it can grow.

So, these are certain applications. The point is that you need to decide what is the problem, what are the properties in your fibers that you want and accordingly, you can perform the heat treatment temperature at higher ramp rates, lower ramp rates, higher temperature, lower temperature and so on.

Yes, you can make fibers in the micro-scale; you can make fibers in the nanoscale. In the nano scale fibers, we are going to talk later on. In principle, during the heat treatment, you should use slightly lower temperature. As I said because the byproducts and defects can anneal out more easily but if it is in the micro-scale, still the effect of surface area is not that strong.

When you have nano-scale fibers, then the surface area effect becomes very strong; especially, when you go below the diameters of 50 nanometer diameters. If you have a smaller than 50 nanometer polymer fiber then the mechanism of carbonization becomes slightly different and you may get more graphitization at lower temperatures.

But in the case of micro scale structures, this effect but compared to bulk structures, still not so prominent that you can drastically reduce your heat treatment temperature. For further reading, there are a lot of books on Carbon fibers and they are very good books, very good articles.

You just do an internet search, you will definitely find several books on Carbon fibers. I have mentioned a couple of papers also because I took some pictures from there.

I followed this book called New Carbons and also this paper by Edie's. These are the papers that I have utilized. There is a lot of reading, further reading about the microstructure of carbon, carbon fibers, especially the pitch-based carbon fibers. Now, in the next couple of lectures, we are going to learn about electro spinning and also, some properties of the polymers that are required for electro spinning.